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THE VOLUME OF EIGHTEEN LIQUIDS AS A FUNCTION OF PRESSURE AND TEMPERATURE.

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TABLE OF CONTENTS.

	Page
Introduction	185
The Method	187
Detailed Data	198
Normal Pentane	198
Iso-pentane	199
Normal Hexane	201
2-methyl Pentane	201
3-methyl Pentane	203
2–2-dimethyl Butane	204
2–3-dimethyl Butane	205
Normal Heptane	206
Normal Octane	207
Normal Decane	208
Benzene	209
C_6H_5Cl	210
C_6H_5Br	211
CCl_4	212
Bromoform	213
Iso-propyl Alcohol	214
Normal Butyl Alcohol	214
Normal Hexyl Alcohol	216
Ether	217
Water	219
Glycerine and Water Mixture	220
Discussion	221
Summary	232

Introduction.

One of the first extended series of measurements of the effects of pressure that I attempted was on the volume of twelve liquids between 20° and 80° C. and up to 12000 kg/cm².[1] Since then I have made many determinations of the compressibility of solids, but have not returned to the question of liquids, in spite of the interest of the subject and the comparatively small number of liquids investigated. My reason for waiting so long before extending the early investigation

has been in large part my desire to improve the method there used. That method was extremely simple: it consisted merely in measuring the motion of the piston by which pressure was produced. There were, however, several unsatisfactory features: the correction for the compressibility of the transmitting medium might be as large or larger than the effect being measured; the correction for the distortion of the cylinder, although small, had to be obtained by a calculatoin which is unsatisfactory because the metal is stressed beyond its elastic limit; there was considerable hysteretic difference between the readings with increasing and decreasing pressure with consequent possibility of error in the mean; and the thermal expansions under pressure were likely to be in error because the pressure measuring gauge was subject to the same changes of temperature as the liquid itself. This last point I felt to be of particular importance; for several speculations an exact knowledge of the limiting behavior of the thermal expansion at high pressures is important, so that it was particularly desirable to devise a method capable of giving this with greater accuracy. After a number of trials, extending over several years, and including work with the free piston piezometer,[2] which at first was very promising, but which had to be discarded because it could not give accurate enough values for the thermal expansion, such a method has been devised, so that the way is now open for the routine measurement of a large number of liquids.

In the following are presented the first of the data obtained in this projected campaign on the determination of the volume of a large number of liquids as a function of pressure and temperature. The twelve liquids chosen for the previous investigation were those which had been previously investigated by Amagat; the reason for this choice was to allow comparison with his results in the pressure range up to 3000 kg, and, particularly, to supplement the results at low pressures by Amagat's measurements, the previous method not being well adapted to give accurate values at low pressures. The liquids of Amagat were, however, in many cases of complex structure, and are not those which would naturally be chosen for their significance in theoretical speculations. In the following an effort has been made to select liquids more "normal" in structure, and therefore of greater theoretical interest. In the first place, a number of hydro-carbons are investigated: normal- and iso- pentane, n- hexane and its four isomers, and n- heptane, n- octane, and n- decane. Five liquids are measured which the theoretical investigations of Hildebrand have

suggested as of interest, namely, C_6H_6, C_6H_5Cl, C_6H_5Br, CCl_4 and $CHBr_3$. The previous work has been supplemented by measurements of iso-propyl and n-butyl alcohols, the previous measurements having included n-propyl and iso-butyl alcohol. Finally, measurements, merely for check purposes, were made on ether and water and a mixture of glycerine and water.

The liquids chosen for this investigation often suffer from the disadvantage that the range open to measurement, particularly at the lower temperature, is small because of freezing under pressure. However, this limitation is unavoidable; many of the liquids of greatest theoretical interest are easily frozen by pressure.

The previous measurements were made at 20°, 40°, 60°, and 80° C. The temperature behavior proved to be very complicated, there being numerous small scale irregularities superposed on the large scale regularities. These small scale irregularities are, however, so complicated that they are not of much present significance for any theory, and in fact they have been entirely ignored in the theoretical speculations of various writers which have been based on these data. I felt therefore that in this new investigation the emphasis should be placed less on these small scale effects, and have accordingly increased the temperature range from 60° to 95°, but have diminished the number of temperatures from four to three, the new measurements being made at 0°, 50°, and 95°. In this way fewer of the small scale phenomena are disclosed, but greater confidence may be felt in the accuracy of the large scale effects, because of the increase of range.

It has also been possible to cover a greater range of material in the same time by decreasing the number of temperatures. A still wider range of temperature would obviously have been desirable, but this would have demanded essential changes and complications in the whole technique, with a corresponding great decrease in the number of substances that could be examined.

The Method.

The fundamental idea of the method is very simple; the liquid to be measured is sealed into a metal "sylphon" (trade name for a flexible metal bellows), which is then exposed to external hydrostatic pressure. The sylphon shortens until the internal pressure is equal to the external, and from a measurement of the shortening, the change of volume of the liquid inside may be obtained. The advantages of this simple scheme are obvious; the separation of the liquid to be

measured from the transmitting liquid is absolute, allowing no contamination; the effect measured is nearly the entire effect, for obviously the corrections are small, and furthermore may be computed with precision, for all the parts involved are subject to hydrostatic pressure and there is no distortion by exceeding the elastic limit; and finally, the pressure gauge may be placed in a vessel separate from that containing the sylphon, so that the temperature of the gauge may be kept independent of the varying temperature of the sylphon, thus eliminating this source of possible error in the previous method of measuring thermal expansion at high pressure.

The method is not entirely smooth sailing, however, but there are several matters, either of construction or function, that require examination. In the first place, there is the question of whether enough distortion can be obtained with the sylphon to permit convenient measurement of the rather large changes of volume involved, amounting to at least 30%. The ordinary sylphon of commerce does not have the requisite flexibility, and furthermore, at the time that this investigation was begun, was not made in sizes small enough to permit its use except by constructing an entire new high pressure plant capable of handling larger volumes. The construction of the necessary tools and jigs for the making of a single small sylphon of the commercial pattern, that is, by forming seamless from a single piece of metal, would have cost $10000, and was therefore prohibitive. The only course open was to build up a sylphon of the desired size by soldering together small sections; this was successfully accomplished, and will be described in detail later. In the second place, there was the fundamental question of whether the interior volume of such a sylphon may not be a complicated function of its length and the hydrostatic pressure. This happily proved not to be the case, but the sylphon has the property that it acts as if it had a fixed effective cross section independent of its extension, so that the change of internal volume may be obtained at once, after the necessary calibration has been made, in terms of its change of length. The check measurements by which this was established will be described in detail later.

The way in which the sylphon is built up in sections is indicated in Figure 1. The individual sections are formed by stamping into a die in a single operation, as indicated in Figure 2. After stamping, the edges of the section are trimmed with a sharp knife. A good many trials were made before the proper dimensions and material were found for the stampings. If the material is too thick, the

resulting sylphon is too stiff; if it is too thin, it cannot be formed without tearing. The material finally adopted was "shim" brass, 0.0015 inches (0.0038 cm.) thick. It was cut into true discs in the lathe for forming, and then was carefully annealed to soften it. The forming operation restores it to just the right amount of springiness. Brass 0.002 inches thick was much too thick, and 0.0012 inches was too thin. Materials unsuccessfully tried were: another grade of brass specially manufactured and recommended for deep drawing, as well as grades of phosphor bronze and nickel silver also made for the same purpose, soft iron, silver, platinum, and copper.

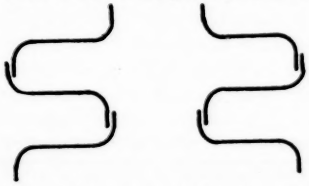

FIGURE 1. Shows the way in which the sylphon is built up in sections.

The sections are held together by first spinning over the edges and then by soldering. A specially built tool of readily suggested design for holding and rotating the sections as they are built up facilitates the assembly. The soldering must be above suspicion. It pays to brighten the edges of the seams with fine emery paper before applying the solder. Minute leaks proved the greatest difficulty in practise; these were fully as likely to be due to flaws in the metal as to imperfections in the soldering, and were often extremely difficult to detect at atmospheric pressure. The best method found for locating a leak at atmospheric pressure was to submerge the sylphon in alcohol while attached to a source of hydrogen at not more than half an atmosphere pressure. The hydrogen gets through fine holes much more easily than air, and alcohol has the advantage of water that it does not deposit on the brass fine bubbles of air from solution. The most satisfactory method of proving that the sylphon is tight is to fill it with a volatile liquid, such as ether or carbon bisulfide, sealing it when the sylphon is stretched so that the liquid will be under a slight excess pressure, and then finding whether the sylphon with its contents changes in weight over an interval of several days. No sylphon which passed this test ever proved defective under pressure.

Considerable skill is necessary in soldering the sections together

so as not to put them in such a state of strain that they will snap from one position to another, like the bottom of an oil squirt, at some stage in the stretching. A sylphon which snaps in this way

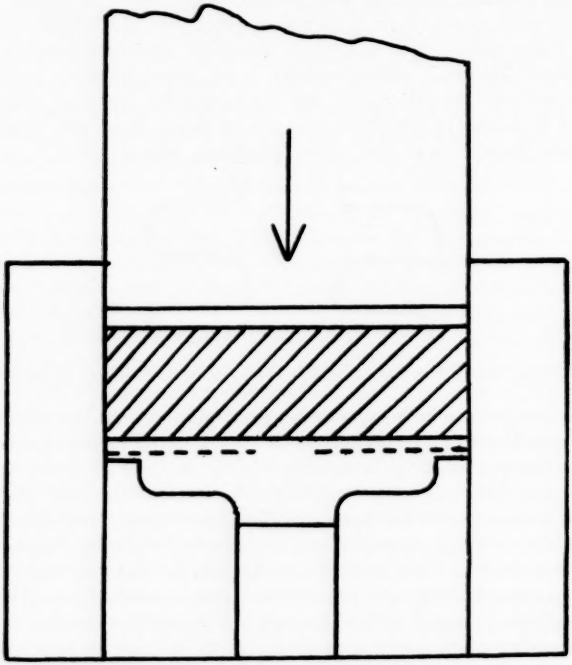

FIGURE 2. Shows the method of forming the sylphon sections by stamping. The thin disc to be formed is indicated by the dotted line. It is forced to the contour of the die by the lead disc, shaded, which is squeezed into the die by the action of the steel piston, indicated by the arrow.

may as well be discarded at once, because the calibration will show jumps in the volume as a function of length, and it is therefore useless for accurate measurements. After some practice my mechanic, Mr. Charles Chase, developed much skill in the production of these sylphons, and is now able to complete one in about half a day; this paper would have been hardly possible without his skillful assistance.

The sylphon as finally constructed consists of nine double sections, of an unextended length of 1 inch (2.5 cm.). The flexibility allows a motion of 0.187 inch (0.475 cm.) in both directions, giving 0.375 inches altogether, or about 32% on the measured volume. The essential parts of the mounting of the sylphon are shown in Figure 3. End pieces are soldered to the sylphon bellows, and the combination is mounted in a brass sleeve which carries the arrangement by which the change of length is measured. This is the conventional sliding contact arrangement, consisting of a manganin wire sliding over an insulated contact. Measurements of the potential difference between the points A and B give the length of the segment AB and so the length of the sylphon to which the wire is attached.

Some sort of a guide has to be provided to constrain the sylphon to shorten and lengthen in the same straight line. This guide is provided by a piston and cylinder integral with the end pieces of the sylphon, playing one within the other, as sufficiently indicated by the drawing. At first the guide was made external to the sylphon, as would naturally suggest itself, but free motion was often interferred with by particles of dirt getting between the bearing surfaces, and the guides were finally put inside with complete success. Complete freedom of motion is obviously a prime requisite, for if the difference of pressure between the inside and the outside of the sylphon reaches much more than half an atmosphere the metal is permanently deformed, and the sylphon must be discarded. In order to avoid seizing of the guides, which often occurs when metal parts in relative motion are made of the same metal, the upper end piece, bearing the piston part of the guide, was made of brass, and the lower part, bearing the cylinder, of copper (not vice-versa because brass is more compressible than copper). To further prevent sticking if any particles of dirt should accidentally be in the sylphon initially, a spiral groove, not shown in the diagram, was cut on the brass piston, in which such particles might lodge. A further advantage gained by placing the guides inside the sylphon is that the internal volume available to the liquid is thereby cut down, thus decreasing the stroke necessary, which otherwise would have been uncomfortably close to the maximum allowable.

The sylphon was filled through the German silver tube at the lower end. During filling the sylphon is first stretched to a definite length and held there with a pin through appropriate holes in the brass sleeve. It is then inverted, a thistle-shape glass containing

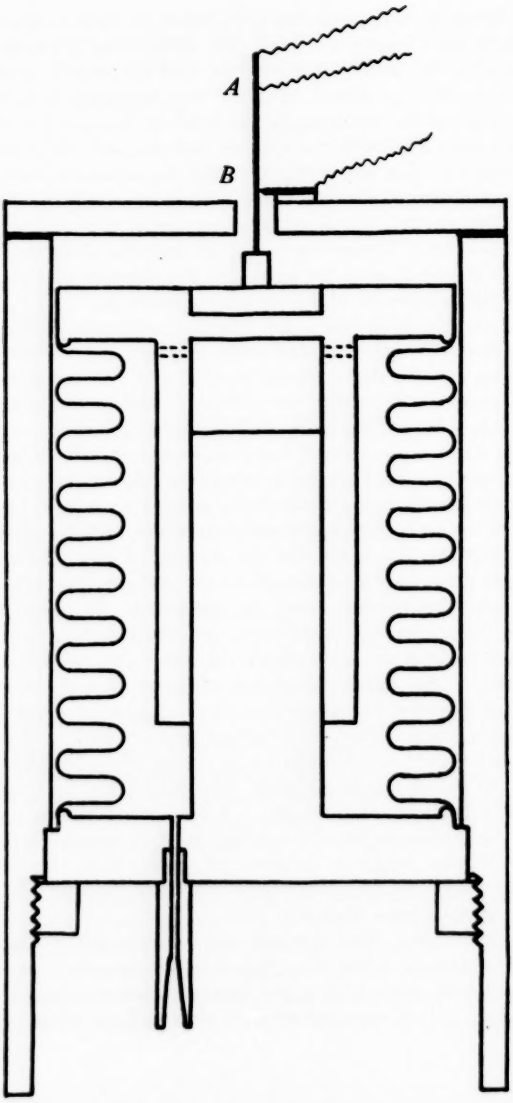

FIGURE 3. The sylphon assembled, with the internal guides and the electrical connections.

the liquid is attached to the German silver tube, and the whole is placed under the receiver of an air pump. The receiver is alternately exhausted and air readmitted until the sylphon is entirely full. The exhaustion also serves the purpose of removing dissolved air from the liquid. During the process of filling, the air must both be removed and readmitted with sufficient slowness to prevent the difference of pressure within and without the sylphon exceeding a safe value. After filling, the German silver tube is filled with a long tapering pin of German silver, and the amount of liquid in the sylphon determined by weighing. The total available volume of the sylphon was about 5 cm.^{3}, and weighings could be made consistent to a fraction of a milligram, so that no appreciable error attaches to the determination of the amount of liquid, After weighing, the sylphon was sealed by soldering into place the German silver pin, the outside of the tube being surrounded with water during the soldering to prevent transmission of heat to the liquid. German silver was used in order to make transmission of heat to the liquid through it as small as possible.

The sylphon thus filled was attached to an insulating three-terminal plug, the various necessary electrical connections were made by soldering, and the whole thing put as one assembly into the high pressure cylinder. This part of the process is so much like that which I have previously employed and described in detail[3] that it is not necessary to go into further detail here.

The first pressure run was almost always made at 0°, starting with the reading at atmospheric pressure, then at a few hundred kilograms, and then at increasing intervals to the maximum pressure which it was judged could be safely reached without freezing, or if there was no danger of freezing, to a maximum of 12000 kg. After reaching the maximum, readings were made with decreasing pressure back to about 500 kg, interspersing the readings with decreasing pressure between those with increasing pressure. The final result was a series of readings separated by intervals of the order of 300 kg at the lower end of the pressure range, and 1000 kg at the upper end. When the apparatus was functioning properly, there was never the slightest hysteresis between the readings with increasing and decreasing pressure, but both lay on the same smooth curve. This constitutes a great advantage over the piston displacement method. It was, however, sometimes necessary to season a new sylphon by a preliminary application of pressure; apparently the soldered seams as left

by the soldering iron are capable of slight permanent deformation on the first application of pressure. The transmitting medium was pure petroleum ether; a liquid like kerosene becomes sufficiently viscous at high pressures to permanently deform the sylphon. Obviously excessive viscosity in the liquid within the sylphon may produce irregular results as well as viscosity in the external transmitting liquid. In fact there does seem a distinct tendency in the following for those liquids to give the most irregular results whose increase of viscosity under pressure is likely to be the greatest, that is, those liquids with the most complicated molecules.

In measuring those liquids whose freezing points under pressure were not known a number of sylphons were ruined by carrying the pressure up to the freezing point. The necessity for caution thus having been impressed, a small amount of freezing often being sufficient to do irreparable damage, the tendency in later work was perhaps to stay farther away from the freezing point than was necessary, and it would probably be possible to materially extend the range of data for a number of the following liquids without freezing. Freezing disclosed itself, not in the sudden decrease of volume that might perhaps at first be expected, but usually by a stationary reading, the guides freezing fast to each other, and the decrease of volume being taken up at the expense of permanent distortion of the sylphon. In all, eleven different sylphons were used in the following measurements.

After completion of the measurements at 0°, temperature was raised to 50° while pressure was maintained at about 500 kg. and a series of readings was made similar to those at 0°, with both increasing and decreasing pressure, except that the maximum pressure possible without freezing was now higher. After the 50° run, temperature was raised to 95°, and a similar series of readings made. In many cases the lowest pressure possible at 95° was somewhat higher than 500 kg., since the thermal expansion, if the pressure had been allowed to get lower, would have been sufficient to extend the sylphon beyond its limit. This accounts for the fact that in the following Tables many of the results given for 95° begin with the 1000 kg value instead of with that for 500 kg. After completion of a run at 95°, check measurements were always made again at 0° and 50° at some low pressure in the neighborhood of 500 kg, in order to be sure that the sylphon had experienced no permanent distortion. This test was practically always met within the errors common to all the readings.

In fact, the perfectly single valued character of the readings was a source of great satisfaction; it was possible to make runs at different temperatures on successive days without paying the slightest regard to the intermediate history of the apparatus. On several occasions a much severer test was successfully passed, in that the sylphon, sealed full with liquid, was removed from the holder, and the entire apparatus disassembled and then put together again, with perfect recovery of the original settings. This is all in striking contrast with the piston displacement method, in which a rigorous schedule of manipulation must be followed in order to reduce the hysteresis phenomena to reproducibility.

The completely single valued character of the readings made it possible to obtain accurate values for the thermal expansions from successive pressure runs at different temperatures, instead of being compelled to adopt the more direct procedure of changing temperature at constant pressure, which would have been much more inconvenient, because pressure is always easier to change than temperature. That the two procedures give identical results was established in a preliminary investigation.

In order to convert the measured changes of length of the sylphon into changes of volume, the effective cross section of the sylphon must be found by special calibration. To do this the sylphon was mounted in a special holder in which it could be shortened or lengthened by measured amounts with a micrometer screw, a graduated and calibrated glass capillary was attached to the German silver outlet tube, the sylphon was filled with kerosene, and the height of the kerosene in the capillary determined as a function of the length as given by the micrometer, making about 20 readings in all. The relation between length and change of volume turned out to be linear to better than 0.1 %, a result very gratifying and not expected. Furthermore, it was established by special trial that the volume is not perceptibly affected by pressure differences between the inside and outside of the sylphon up to as much as one-half atmosphere, which is close to the pressure of permanent deformation.

The manganin wire by which the length of the sylphon was determined was also specially calibrated. This again was done by moving it with a micrometer screw over a fixed contact in a specially constructed appliance, which need not be described in detail. Samples of wire were selected which were uniform to considerably better than 0.1%, so that no corrections had to be applied for lack of uniformity.

As indicated in Figure 3, the manganin wire was mounted detachably on the sylphon, so that the same wire could be used with several sylphons, considerably simplifying the manipulations and the calculations.

There are a number of small corrections which must be applied to the readings. The actual formulas for the corrections are somewhat complicated, and will not be written out in detail, since they are simple enough in general idea. The corrections are mostly for the compressibility of the various parts of the apparatus, and include the following.

(1) Correction for the compressibility of the brass sleeve which carries the contacts. Three different sleeves were made and used interchangeably at different times. These were all made from the same bar of brass. Its compressibility was determined by special experiment in the "lever" piezometer, and had the following values

$$\text{At } 30°, \quad -\Delta V/V_0 = 9.207 \times 10^{-7}p - 6.42 \times 10^{-12}p^2.$$

$$\text{At } 75°, \quad -\Delta V/V_0 = 9.309 \times 10^{-7}p - 5.79 \times 10^{-12}p^2.$$

(2) Correction for the compressibility of the brass part of the guide. This was made from the same bar as the sleeve, and therefore the correction has the value just given.

(3) Correction for the compressibility of the copper part of the guide. The compressibility of copper has been previously determined,[4] and the previous value was used.

(4) Correction for the compressibility of the manganin wire. This has also been previously determined, and the previous value was used.

(5) Correction for the compressibility of the sheet brass of which the sylphon is constructed. This was not independently measured, as it would have been difficult. I assumed that its compressibility is the same as that of the brass of the sleeve; the correction is in any event small, and commercial grades of brass do not differ by large amounts, and I believe the error made by the assumption to be inappreciable.

In addition to the various corrections for compressibility, there is a correction for the change of resistance of the manganin wire under pressure. This is the largest of the corrections, and it was determined by direct measurement on the identical piece of wire used at the three temperatures. The following results were found for the pressure coefficient of resistance: At 0°, 2.288×10^{-6}; at 50°, 2.311×10^{-6}; and at 95°, 2.289×10^{-6}.

There are also corrections for the thermal expansion of various parts of the apparatus on changing temperature. For these, values listed in various tables for brass, copper, and manganin were used, and are accurate enough. The temperature coefficient of resistance of the manganin wire at atmospheric pressure was also specially determined. The maximum variation in the constants of the apparatus due to changes of temperature in the range is about 1.5 parts in 1000. The maximum net correction for pure pressure effects on the runs at constant temperature was not much more than 2%, and the maximum net correction on the thermal expansion at constant pressure 5 or 6%. It is thus evident that as far as magnitude of corrections is concerned, the sylphon method is very greatly superior to the previous method of piston displacement.

The method of computation was first to plot the resistance readings as given by the potentiometer on a large scale on millimeter paper, 1000 kg on the scale of abscissas corresponding to 5 cm on the graph. Smooth curves were then drawn through the observed points, and the resistance read off at even intervals of 500 or 1000 kg. The changes of volume corresponding to these even intervals were then calculated with the aid of the various correction formulas. The results so obtained were the actual losses of volume in cm^3 reckoned from the volume at 0° and atmospheric pressure as fiducial. To convert this into fractional changes of volume in terms of the volume at 0° and atmospheric pressure as unity, the density at the fiducial point must be known. This could usually be taken from tables, and usually from International Critical Tables. The values thus used in the final reduction will be given in detail in the following for each individual liquid. The volumes at atmospheric pressure at 50° and 95° were also taken from the tables when possible; this was necessary because, as already explained, the sylphon readings often could not be made at atmospheric pressure at these two temperatures because the thermal expansion was too great, or else because the vapor pressure was above atmospheric.

There are several substances in the list, however, for which the density and thermal expansion at atmospheric pressure has apparently not been determined, notably the isomers of hexane. For these substances the density and thermal expansion at atmospheric pressure was determined by special experiment. For this purpose an alcohol thermometer was emptied, and used as densitometer and dilatometer. The bulb and stem were calibrated by filling with weighed amounts of

mercury, and the stem was calibrated for uniformity with a moving length of mercury. Measurements of the volumes of the various liquids were made at three temperatures: 0°, a temperature about 10° below the boiling point, and a temperature half way between the maximum and 0°. Readings were made with both increasing and decreasing temperature as check; this check was always perfect to the limit of reading, which was 0.1° on the scale of the original alcohol thermometer. The results were put in the form of a second degree series in the temperature, and are given in the following. The density was determined by weighing the dilatometer when filled to a known mark at a definite temperature and when empty. The quantities of liquid used were of the order of 1 cm^3, and weighings were to 0.1 milligram, so that the density should be accurate to perhaps 1/30%. I felt that there was no point in trying for greater precision unless a much more exhaustive examination was made than was practical of the purity and reproducibility of the liquids.

If at any time in the future it should be found that better values for the densities or thermal expansions at atmospheric pressure are available, the relative volumes given in the following Tables can be readily corrected in accordance with the improved information. In the Tables the differences of volume from the fiducial volume at 0° and atmospheric pressure are the immediate result of the pressure measurements. If for instance, the future best value for the density at the fiducial point should turn out to be 1% less than the value assumed in the calculations, then the differences of volume reckoned from the fiducial point should all be decreased by 1%, increasing the actual volumes at any definite temperature and pressure. For example, a volume tabulated as 0.900 should be corrected to 0.901 in the hypothetical case.

The liquids measured in the following were obtained from various sources, selected for the greatest probable purity, and will be given in the detailed description. In general, the liquids were used as obtained, with no attempt at further purification; previous experience has shown that compressibility is insensitive to small amounts of impurity.

The detailed presentation of the data for the various liquids now follows.

Detailed Data.

Normal Pentane. The material was from Kahlbaum, their purest, provided in a sealed glass container. The runs at three temperatures

and the return check readings were made without incident of any kind on three successive days. The average departure of a single one of the 46 observed points from the smooth curves was 0.11% of the maximum effect.

The final values for the volume are given in Table I. For the

TABLE I.

RELATIVE VOLUME OF N-PENTANE.

Pressure kg./cm.²	Temperature 0°	50°	95°
0	1.0000	1.0837	1.1869
1,000	.9021	.9395	.9768
2,000	.8546	.8820	.9078
3,000	.8229	.8454	.8671
4,000	.7997	.8193	.8371
5,000	.7811	.7985	.8125
6,000	.7647	.7807	.7933
7,000	.7506	.7657	.7775
8,000	.7381	.7520	.7641
9,000	.7281	.7409	.7527
10,000	.7192	.7316	.7433

density at atmospheric pressure the following formula was used from International Critical Tables (abbreviated in the following as I. C. T.)

$$\text{Density} = 0.64539 - 0.9398 \times 10^{-3}t - 0.6243 \times 10^{-6}t^2 - 7.53 \times 10^{-9}t^3.$$

The two temperatures, 50° and 95°, listed in the Table are above the boiling point, which is 36°.2. The volumes given in Table I at atmospheric pressure at 50° and 95° were obtained by formal substitution in the formula for density, and must be used merely to get the approximate location of the 50° and 95° volumes at the lower pressure end of the range.

Iso-pentane. This material was from the Eastman Kodak Co., provided in a sealed glass container. Runs were made without incident at 0° and 50°, but at 95° there was an explosion at 10000 kg, so that readings with decreasing pressure were not made at this temperature, nor were the return check readings made. The average departure from a smooth curve of a single one of the 37 readings was 0.17% of the maximum effect.

An experimental point was obtained at 7200 kg at 0° that lay off

the curve by three or four times as much as any other point, and was taken as indicating the beginning of freezing. Because of possible damage to the sylphon, the matter was not investigated further. Further consideration makes it very improbable, however, that this irregularity was actually due to freezing, since the melting temperature at atmospheric pressure of iso-pentane is about 28° lower than that of normal pentane, and normal pentane has been carried to 10000 kg at 0° without a trace of freezing. Of course it is not impossible that the melting curves should cross, and there are known examples of it, but certainly 7200 kg should not be accepted as the melting pressure at 0° of iso-pentane without further confirmation.

The values for the relative volumes are given in Table II. The volume of i-pentane as a function of temperature at atmospheric pressure does not seem to be recorded in the literature, and it was therefore specially determined by the method already described. The following results were found:

$$\text{Density} = \frac{.6406}{1 + .001527t + 3.21 \times 10^{-6}t^2}.$$

Because of the low boiling point, the temperature interval was only from 0° to 23°.5, so that the temperature coefficients in this formula have no great accuracy. The relative volumes are given in Table II. The volumes at 50° and 95° at atmospheric pressure were ob-

TABLE II.

RELATIVE VOLUME OF I-PENTANE.

Pressure	Temperature		
kg./cm.²	0°	50°	95°
0	1.0000	1.0843	1.1741
500.	.9383	.9883	
1,000	.9028	.9415	.9809
1,500	.8775	.9084	.9405
2,000	.8571	.8845	.9119
3,000	.8264	.8490	.8712
4,000	.8025	.8222	.8403
5,000	.7830	.8014	.8178
6,000	.7670	.7850	.8002
7,000	.7534	.7729	.7863
8,000		.7592	.7706
9,000		.7474	

tained by formal extrapolation of the formula above, and the remarks already made concerning n-pentane apply here also.

Normal Hexane. The material was obtained from the Eastman Kodak Co. Complete runs at three temperatures and the return check runs were made without incident on three successive days. Discarding two points, in which there were probably errors of recording, the average departure from a smooth curve of a single one of the remaining 42 readings was 0.22% of the maximum effect.

The maximum pressure at which readings were attempted at 0° was 6000 kg. From the atmospheric freezing point and a previous determination of the freezing point at 30° as 10600 kg. this was roughly estimated to be the highest safe pressure.

The relative volumes are given in Table III. For the density at

TABLE III.

RELATIVE VOLUME OF N-HEXANE

Pressure	Temperature		
kg./cm.²	0°	50°	95°
0	1.0000	1.0712	1.1535
1,000	.9191	.9567	
2,000	.8763	.9048	.9304
3,000	.8472	.8720	.8914
4,000	.8259	.8472	.8629
5,000	.8068	.8262	.8404
6,000	.7905	.8091	.8225
7,000		.7943	.8071
8,000		.7817	.7942
9,000		.7707	.7824
10,000		.7615	.7723
11,000		.7529	.7632

atmospheric pressure the following formula from I. C. T. was assumed:

$$\text{Density} = 0.6769 - 0.8486 \times 10^{-3}t - 1.084 \times 10^{-6}t^2 + 0.164 \times 10^{-9}t^3$$

The boiling point is 69°, so that the legitimate use of the formula is restricted to temperatures lower than this; the volume at 95° at atmospheric pressure in the table was obtained by formal substitution in the formula.

2-methyl Pentane. For this isomer of hexane, as well as for the following three others, I am exceedingly indebted to Mr. T. A. Boyd

of the Fuel Research Section of the General Motors Corporation. I am also indebted to Professor J. B. Conant for putting me in touch with Mr. Boyd.

The first attempt with this substance at 0° had to be discontinued at 4500 kg because of minor trouble with the insulation, which was speedily repaired. After reassembling, the three regular runs at three temperatures were made on three successive days. The return check readings were inadvertently omitted. The average departure from a smooth curve of a single one of the 42 readings was 0.20% of the maximum effect.

The maximum pressure attempted at 0° was 6000 kg. This was merely estimated as the safe maximum from relative boiling and melting points at atmospheric pressure as compared with n-hexane; no evidence of freezing under pressure was found during the experiment.

The relative volumes are given in Table IV. The density at

TABLE IV.

RELATIVE VOLUME OF 2-METHYL PENTANE.

Pressure	Temperature		
kg./cm.²	0°	50°	95°
0	1.0000	1.0736	1.1549
500	.9460	.9930	
1,000	.9131	.9496	.9851
1,500	.8896	.9203	.9496
2,000	.8711	.8976	.9227
3,000	.8419	.8638	.8826
4,000	.8191	.8382	.8552
5,000	.8009	.8184	.8336
6,000	.7844	.8023	.8179
7,000		.7878	.8022
8,000		.7754	.7886
9,000		.7644	.7763
10,000		.7538	.7658
11,000		.7450	.7564
12,000			.7484

atmospheric pressure, which had to be determined by special experiment as already mentioned, was:

$$\text{Density} = \frac{0.6720}{1 + 0.001297t + 3.52 \times 10^{-6}t^2}.$$

The temperature range of the density measurements was 52°; the value given in the table at atmospheric pressure at 95° is merely a formal extrapolation.

3-methyl Pentane. This also was obtained from the General Motors Corporation. The only incident during the run was a leak in the connecting pipe, which developed at 50° at about 9000 kg. because the washers had been used too long without changing. Pressure was released, the apparatus reassembled, and the run continued. The part of the run below 9000 at 50° was repeated, in perfect agreement. The usual return check readings were made after the three runs at constant temperatures; all measurements were made on three successive days. The average departure from a smooth curve of a single one of the 55 readings was 0.19% of the maximum effect.

The maximum pressure attempted at 0° was much higher than for the two preceding isomers, 11000 against about 6000. That this was safe was suggested by the much lower melting point at atmospheric pressure; no sign of freezing was detected.

The relative volumes are given in Table V. The density at atmos-

TABLE V.

RELATIVE VOLUME OF 3-METHYL PENTANE.

Pressure	Temperature		
kg./cm.²	0°	50°	95°
0	1.0000	1.0727	1.1530
500	.9434	.9884	
1,000	.9120	.9471	.9815
1,500	.8879	.9189	.9462
2,000	.8689	.8971	.9205
3,000	.8408	.8630	.8824
4,000	.8200	.8379	.8553
5,000	.8022	.8189	.8342
6,000	.7866	.8026	.8158
7,000	.7723	.7888	.8006
8,000	.7592	.7761	.7876
9,000	.7476	.7647	.7753
10,000	.7372	.7544	.7649
11,000	.7276	.7455	.7550
12,000		.7373	.7452

pheric pressure, as found by special experiment, was:

$$\text{Density} = \frac{0.6835}{1 + 0.001285t + 3.43 \times 10^{-6}t^2}.$$

The volume given in the table at 95° at atmospheric pressure is a formal extrapolation.

One striking feature of the results with this substance is the way in which the isotherm for 50° is displaced away from the 0° isotherm and toward the 95° isotherm at the upper end of the pressure range. There can be little question but that this effect is genuine, the effect being much beyond the error of the measurements, and the irregularity in the points in the neighborhood being on the whole less than the average.

2–2-dimethyl Butane. This, like the two preceeding isomers, was obtained from General Motors. On the first attempt at 0° there was a leak in the manganin gauge plug at 3000, but this was successfully repaired, and the run continued, the points after reassembly checking those before. Three regular runs were made on three successive days. The return check readings were not made because after the run at 95° the pressure was inadvertently allowed to get so low that the sylphon blew up by boiler pressure. This was particularly unfortunate, because the quantity of this isomer available was smaller than that of any of the others, and there was not enough left for the dilatometer and density measurements. The average departure from a smooth curve of a single one of the 40 readings was 0.15%.

The freezing pressure of this isomer was so unexpectedly low that I was not successful in guessing its location, but freezing was encountered at each of the three temperatures. At 0° freezing was observed at 5400 kg., at 50° at 8000, and at 95° at 10800. It is not pretended that these give accurately the coördinates of the melting curve; it is merely certain that at each temperature the equilibrium pressure is lower than that given. Fortunately, no permanent damage was done to the sylphon by the amount of freezing that took place, as was proved by the perfect check between the points obtained with increasing and decreasing pressure.

The relative volumes are given in Table VI. These values are only approximate, because, as already explained, no measurements were made on the density or dilatation of this isomer. In calculating the values in the table, the density at 0° was assumed to be 0.6693. This value was estimated, on the assumption that the change of density on passing from 2–3 dimethyl butane to 2–2-dimethyl butane

TABLE VI.

RELATIVE VOLUME OF 2–2-DIMETHYL BUTANE.

Pressure	Temperature		
kg./cm.²	0°	50°	95°
0	1.0000		
500	.9496	.9955	.
1,000	.9154	.9517	.9824
1,500	.8919	.9232	.9478
2,000	.8737	.9016	.9218
3,000	.8473	.8703	.8855
4,000	.8260	.8464	.8594
5,000	.8083	.8269	.8392
6,000		.8106	.8223
7,000			.8079
8,000			.7958
9,000			.7850
10,000			.7756

would be the same as on passing from 3-methyl pentane to 2-methyl pentane. No attempt was made to estimate the dilation, and these places are left vacant in the table.

2–3-dimethyl Butane. This, the last of the isomers of hexane, was also obtained from General Motors. Several vicissitudes were encountered during the runs with this substance. At the termination of the 0° run short circuits developed in the manganin gauge and the sylphon circuits. These were repaired, the apparatus set up again, and perfect check readings obtained at 0°. The 50° run was now completed without incident. The readings from the beginning of the 95° run were unsteady. The matter finally grew so bad that the apparatus was dismantled, and the sylphon set up again in another holder, thus of course changing by a slight amount the zero reading. The 95° run was now completed without incident. The usual check readings at 50° and 0° were finally taken; the difference between these agreed with the value found in the previous holder, as it should. The difference between the 50° readings with the old and new holders gives the difference of zero readings between the two holders. The average departure from a smooth curve of a single one of the 45 readings available for locating the isotherms was 0.23%.

At 0° freezing was probably encountered at 6200 kg.; no permanent distortion in the sylphon seemed to be the result of this freezing. At the other temperatures there was no trace of freezing.

The relative volumes are given in Table VII. The density at

TABLE VII.

RELATIVE VOLUME OF 2–3-DIMETHYL BUTANE.

Pressure	Temperature		
kg./cm.²	0°	50°	95°
0	1.0000	1.0722	1.1496
500	.9485	.9930	
1,000	.9147	.9503	.9841
1,500	.8909	.9202	.9478
2,000	.8695	.8960	.9198
3,000	.8395	.8633	.8836
4,000	.8180	.8383	.8562
5,000	.8004	.8186	.8340
6,000	.7855	.8028	.8162
7,000		.7881	.8008
8,000		.7747	.7874
9,000		.7624	.7757
10,000		.7509	.7645
11,000			.7546

atmospheric pressure, found by special experiment, was:

$$\text{Density} = \frac{0.6808}{1 + .001311t + 2.67 \times 10^{-6}t^2}.$$

The volume at atmospheric pressure at 95° listed in the table is merely a formal extrapolation.

Normal Heptane. The material was obtained from the Eastman Kodak Co. The runs at three temperatures and the return check readings were made on three successive days without incident. This substance was one of the very few for which the return check readings were not satisfactory. The interval between the 0° and the 50° isotherms was satisfactorily checked, but there is some doubt about the relative separation of the 50° and the 95° isotherms. The values given in the table are those which the internal evidence suggests as most probable, but it is barely possible that all the volumes of the 95° isotherm should be decreased by 0.0019. The average departure from a smooth curve of a single one of the 41 readings was 0.12% of the maximum effect.

No trace of freezing was found. The maximum safe pressure was estimated from the atmospheric melting point and the known behavior of n-hexane.

The relative volumes are given in Table VIII. The value of

TABLE VIII

RELATIVE VOLUMES OF N-HEPTANE.

Pressure	Temperature		
kg./cm.²	0°	50°	95°
0	1.0000	1.0633	1.1350
500	.9535	.9972	
1,000	.9223	.9584	.9919
2,000	.8813	.9083	.9337
3,000	.8531	.8753	.8954
4,000	.8315	.8508	.8676
5,000	.8145	.8312	.8457
6,000		.8146	.8276
7,000		.8001	.8125
8,000		.7875	.7992
9,000		.7763	.7870
10,000		.7659	.7762
11,000			.7660

density used in the calculations was that given in I. C. T. and is:

$$\text{Density} = 0.70048 - 0.8476 \times 10^{-3}t + 0.1880 \times 10^{-6}t^2 - 5.23 \times 10^{-9}t^3.$$

The normal boiling point of heptane is 98°.4, so that the 95° value given in the table at atmospheric pressure is in the range of actual values.

Normal Octane. This material was obtained from the Eastman Kodak Co. The measurements on this were made early in my experience, with a new sylphon, and before the necessity for seasoning a new sylphon to the highest pressure was recognized. There were considerable irregularities on the first applications, so that it was desirable to repeat some of the runs. Two runs were made at 0°, two at 50°, and one at 95°. The first run at 0° was the most irregular, and was not used in the calculations. However, the mean of the points of this discarded run lay on the curve obtained later, and for this reason the return check readings were thought to be unnecessary. The first run at 50° showed less irregularity than the first at 0°, the sylphon by now having been fairly well seasoned, although the maximum pressure had not been reached, and all except two of the points of the first 50° run as well as all of the second were used in the

final calculation. The highest point at 95° was also irregular and probably for the same reason. Except for the discarded points just mentioned in detail, the average departure from a smooth curve of a single one of the remaining 50 points was 0.24% of the maximum effect.

No irregularity was found at the highest pressures of the second runs at 0° and 50°. The freezing pressures at 30° and 75° have been previously determined, so that there were data at hand to make it possible to stay within the maximum safe pressure.

The relative volumes are given in Table IX. The density assumed

TABLE IX.

RELATIVE VOLUMES OF N-OCTANE.

Pressure	Temperature		
kg./cm.²	0°	50°	95°
0	1.0000	1.0595	1.1230
500	.9572	1.0005	
1,000	.9311	.9654	.9943
2,000	.8924	.9200	.9422
3,000	.8640	.8882	.9068
4,000		.8639	.8802
5,000		.8428	.8592
6,000		.8251	.8416
7,000		.8103	.8267
8,000			.8134
9,000			.8014
10,000			.7915

in the calculation is that given in I. C. T.:

$$\text{Density} = 0.71848 - 0.8239 \times 10^{-3}t + 0.4459 \times 10^{-6}t^2 - 5.293 \times 10^{-9}t^3.$$

Normal Decane. This was obtained from the Eastman Kodak Co. The initial attempt at 50° was not good because of trouble with the insulation of the manganin gauge. The check readings were made several days after the completion of the regular runs, with the same filling of the sylphon, but with a different holder. The average departure from a smooth curve of a single one of the 34 readings was 0.29% of the maximum effect. This irregularity is apparently a little greater than usual; it is really not so, but the appearance is due to the smaller range possible with this material.

Freezing was not encountered on any of the runs. The safe limits were estimated from the known freezing point at atmospheric pressure and the behavior under pressure of the other hydro-carbons. The relative volumes are given in Table X. In calculating the

TABLE X.

RELATIVE VOLUMES OF N-DECANE

Pressure	Temperature		
kg./cm.^{2}	0°	50°	95°
0	1.0000	1.0530	1.1083
500	.9646	1.0029	
1,000	.9383	.9683	.9952
1,500		.9454	.9664
2,000		.9263	.9466
3,000		.8952	.9146
4,000		.8714	.8880
5,000			.8675
6,000			.8481
7,000			.8341
8,000			.8215

results the following formula for the density given in I. C. T. was used:

$$\text{Density} = 0.7455 - 0.7293 \times 10^{-3}t - 0.371 \times 10^{-6}t^2.$$

Benzene. This was Kahlbaum's purest grade, prepared for molecular weight determinations. The pressure range open to investigation with this liquid is very small because of the high freezing point; however the importance of the liquid in various theoretical speculations justified its measurement. The melting curve had been previously exactly determined, so that the maximum safe pressure was known without any guess work. Runs were made at 50° and 95°, and a rather larger number than usual of return check readings were made at 50° without incident. The average departure of a single one of the 25 readings from smooth curves was 0.25% of the maximum effect.

The relative volumes are shown in Table XI. For the density at atmospheric pressure the formula of I. C. T. was used:

$$\text{Density} = 0.90005 - 1.0636 \times 10^{-3}t - 0.0376 \times 10^{-6}t^2 - 2.213 \times 10^{-9}t^3.$$

In Table XI unit volume is taken as the volume at 0°, obtained by extrapolating with the density formula from the melting point down to 0°. In the pressure measurements the volume was not actually measured at atmospheric pressure at 50°, but was obtained by graphical extrapolation from the lowest pressure reading, which was at 370

TABLE XI.

RELATIVE VOLUMES OF BENZENE.

Pressure kg./cm.²	Temperature 50°	95°
0	1.0630	1.1295
500	1.0160	
1,000	.9841	1.0201
1,500	.9591	.9916
2,000		.9684
2,500		.9494
3,000		.9325
3,500		.9177

kg. Such an extrapolation is not very certain, so that it is possible that there may be a slight error in the table in the volume difference between 0 and 500 kg at 50°. The relative volumes in the table at 50° from 500 kg on are based on direct measurement without extrapolation, and these should be relatively exact in terms of the volume at 500 kg and 50° (1.0160), independent of any error in the extrapolated interval.

The volume of benzene has been previously measured by Essex at a number of temperatures between 0° and 100° up to 3000 kg. At the higher temperature the agreement between his results and mine is usually good to one in the third decimal place. At 50° the disagreement is greater, being 3 or 4 in the third place at 500, 1000, and 1500 kg, and 1 in the second place at atmospheric pressure. His volumes are consistently lower than mine.

C_6H_5Cl. This was Kahlbaum's purest. Regular runs at the three temperatures and the return check readings were made on two successive days with no incident. The average departure from smooth curves of a single one of the 39 readings was 0.09%, the measurements on this material being among the most regular of those obtained.

Freezing was not encountered at any temperature.

The relative volumes are given in Table XII. In the calculation

TABLE XII.

RELATIVE VOLUME OF CHLORO-BENZENE.

Pressure	Temperature		
kg./cm.²	0°	50°	95°
0	1.0000	1.0502	1.1013
500	.9737	1.0170	
1,000	.9541	.9882	1.0215
1,500	.9380	.9673	.9955
2,000	.9244	.9511	.9755
2,500	.9127	.9384	.9595
3,000		.9268	.9463
4,000		.9068	.9247
5,000		.8903	.9072
6,000		.8762	.8924
7,000		.8652	.8794
8,000			.8675
9,000			.8580
10,000			.8487
11,000			.8406

the density given in I. C. T. was used:

$$\text{Density} = 1.12782 - 1.0664 \times 10^{-3}t - 0.2463 \times 10^{-6}t^2 - 0.53 \times 10^{-6}t^3.$$

C_6H_5Br. This was Kahlbaum's purest. The 0° and the 50° measurements were made without incident. The 95° run, however, as only partially completed, and then measurements were interrupted for nearly three weeks by the illness of my assistant. After this time the 95° run was resumed, repeating the points formerly obtained, and also making the return check readings at 50° and 0°, all in perfect consistency with the first measurements. This constitutes a rather severe test of the reproducibility and single valuedness of the measurements.

Freezing was not encountered at any temperature.

The relative volumes are given in Table XIII. The density used in the calculation was that given in I. C. T.:

$$\text{Density} = 1.5223 - 1.345 \times 10^{-3}t - 0.24 \times 10^{-6}t^2 + 0.76 \times 10^{-9}t^3.$$

The range of application of this formula given in I. C. T. is 0° to 80°. The value at 95° at atmospheric pressure must therefore be regarded

TABLE XIII.

RELATIVE VOLUMES OF BROMO-BENZENE.

Pressure	Temperature		
kg/cm.²	0°	50°	95°
0	1.0000	1.0467	1.0940
500	.9763	1.0125	
1,000	.9570	.9891	1.0169
1,500	.9409	.9697	.9953
2,000		.9527	.9765
3,000		.9261	.9460
4,000		.9047	.9229
5,000		.8860	.9033
6,000			.8868
7,000			.8726
8,000			.8604
9,000			.8501

in the nature of an extrapolation, although not nearly so hazardous an extrapolation as one beyond the boiling point.

CCl_4. This was Kahlbaum's purest. The region open to measurement is very small because of the unusually steep melting curve. No run was attempted at 0°, because, although the normal melting temperature is − 23°, the freezing pressure at 0° is only about 500 kg. Regular readings at 50° and 95° and the return check readings were made without incident in one day. The average departure from smooth curves of a single one of the 21 readings was 0.15%. If allowance is made for the smallness of the range, the regularity is rather better than usual.

The relative volumes are given in Table XIV. The density at

TABLE XIV

RELATIVE VOLUMES OF CARBON TETRACHLORIDE.

Pressure	Temperature	
kg./cm.²	50°	95°
0	1.0000	
500	.9519	.9928
1,000	.9192	.9540
1,500	.8962	.9262
2,000		.9049
2,500		.8872
3,000		.8726
3,500		.8603

atmospheric pressure is given by I. C. T., as:

$$\text{Density} = 1.63255 - 1.9110 \times 10^{-3}t - 0.690 \times 10^{-6}t^2,$$

restricted to the range 0° to 40°. However, I used the formula by extrapolation to 50°, and the values in the table are based on the density so obtained. The actual volume was not measured at atmospheric pressure at 50°, but was obtained by extrapolation from the lowest pressure, 130 kg. The volume interval between 0 and 500 kg at 50° in the table is therefore subject to slight uncertainty, and the remarks made with regard to benzene apply.

Bromoform. This was obtained from Kahlbaum. The normal melting point is at +7°.7, so that the possible pressure range was very narrow. A regular run was made at 50°, and on the same day at 95° good points with increasing pressure were obtained, but the decreasing pressure points lay further and further from the curve, and on taking the apparatus apart it was found that the sylphon had developed a leak. On allowing it to stand for several days in the room, the sylphon fell completely to pieces, the bromoform exerting some corrosive action. I am informed by my colleagues among the chemists that this is to be expected. No attempt was made to repeat the run. The average departure from a smooth curve of a single one of the 24 readings up to the maximum pressure at 95° was 0.74% of the maximum effect. This large irregularity is mostly due to the smallness of the range; if the range had been normal, the irregularity would have been only 0.25%, not much larger than usual. There is no reason to think that the results obtained before the leak developed are not essentially correct.

No trace of freezing was encountered.

The relative volumes are given in Table XV. The specific volume

TABLE XV.

RELATIVE VOLUMES OF BROMOFORM

Pressure kg./cm.²	Temperature 50°	95°
0	1.0000	1.0427
500	.9628	.9993
1,000	.9369	.9662
1,500	.9158	.9418
2,000		.9225
2,500		.9063
3,000		.8915
3,500		.8782

as a function of temperature at atmospheric pressure is given in a paper by A. and J. Shuman[6] as:

$$V = 0.34204[1 + 9.0411 \times 10^{-4}(t - 7.7) + 6.766 \times 10^{-7}(t - 7.7)^2].$$

Their range was 7°.7 to 50°. I used the formula by extrapolation to 95°. At 50° the volume was not measured at pressure lower than 300 kg, and the volume interval between 0 and 500 kg at 50° given in the table is therefore based on an extrapolation and may be somewhat uncertain. The remarks already made concerning benzene and CCl_4 apply.

Iso-propyl Alcohol. This was originally obtained a number of years ago from Kahlbaum. It had been standing in a cork stoppered bottle and may have absorbed moisture in the intervening time. It was therefore redistilled twice in a fractionating column immediately before the compressibility measurements. As already stated, the reason for including this substance was that measurements had already been made on n-propyl alcohol in the preceding series. The first run at 0° gave highly irregular readings, doubtless because this was a fresh sylphon, not previously seasoned. The runs at 50° and 95° were of normal regularity. The run at 0° was then repeated, with regular readings except at the maximum, 8000 kg, where there was a slight irregularity that had the appearance of freezing. Pressure was not pushed higher for fear of loosing the points already obtained; the points with decreasing pressure lay on a smooth curve with the increasing pressure points. It is somewhat puzzling to understand why on the first application of pressure 10000 was reached at 0° with no appearance of freezing; there is, of course, the possibility of a sub-cooling effect, which may be very capricious. The succession of the melting points of the alcohols at atmospheric pressure would not make it surprising to find freezing at 0° below 12000 kg.

Discarding the first run at 0°, the average departure from smooth curves of a single one of the remaining 42 readings was 0.17%.

The relative volumes are given in Table XVI. The calculations are based on the formula for density given in I. C. T.:

$$\text{Density} = 0.8014 - 0.809 \times 10^{-3}t - 0.27 \times 10^{-6}t^2.$$

Normal-butyl Alcohol. The material was recently obtained from Kahlbaum, and was used without further purification. Considerable trouble was found with this material because of unusual freezing phenomena, and five runs in all were made at 0°, before satisfactory

TABLE XVI.

RELATIVE VOLUMES OF I-PROPYL ALCOHOL.

Pressure	Temperature		
kg./cm.²	0°	50°	95°
0	1.0000	1.0540	1.1097
500	.9630	1.0056	
1,000	.9387	.9725	1.0112
1,500	.9200	.9485	.9807
2,000	.9040	.9296	.9562
3,000	.8769	.8995	.9218
4,000	.8571	.8765	.8961
5,000	.8398	.8579	.8750
6,000	.8244	.8415	.8572
7,000	.8116	.8279	.8419
8,000	.8002	.8159	.8289
9,000	.7901	.8052	.8168
10,000	.7813	.7948	.8062
11,000		.7861	.7971
12,000		.7784	.7894

results were obtained, the first two with a different filling of the apparatus from the others. I had not anticipated any trouble from the freezing of this alcohol, so that pressure was pushed to 12000 on the first run at 0°. But the reading at 12000 was the same as at 10200, showing that freezing had taken place somewhere in the interval. On the next application the pressure was kept below 10000, but an irregularity at the maximum, 9700, showed that freezing had again taken place. On the next two applications of pressure freezing phenomena were successively found at 7900 and probably at 7000 kg, and it was only on the fifth attempt, when pressure was not pushed higher than 5000, that no freezing was encountered. The successive lowering of the freezing pressure may have been due to a subcooling effect, there being nuclei of the solid phase left in the liquid, making the new formation of the solid easier at every successive attempt, as might be suggested by my previous experience with ice VI, or it may be that with each successive freezing there was increasing purification of part of the alcohol, complete remixing and diffusion of the segregated impurity being prevented by the high viscosity under pressure and the complex geometrical shape of the sylphon.

The two other runs at 50° and 95° and the return check readings were made without further incident. The average departure from

a smooth curve of a single one of the 44 readings of the good runs was 0.27%. This is somewhat higher than usual, and is probably an effect of the freezing, although not the slightest damage to the sylphon was visible to the eye.

The relative volumes are given in Table XVII. The calculations

TABLE XVII.

RELATIVE VOLUMES OF N-BUTYL ALCOHOL.

Pressure	Temperature		
kg./cm.²	0°	50°	95°
0	1.0000	1.0455	1.0907
500	.9697		
1,000	.9459	.9779	
1,500	.9264	.9557	.9801
2,000	.9111	.9372	.9595
3,000	.8874	.9087	.9276
4,000	.8681	.8867	.9033
5,000	.8512	.8684	.8834
6,000		.8530	.8667
7,000		.8390	.8519
8,000		.8269	.8388
9,000		.8153	.8277
10,000		.8076	.8174
11,000			.8082
12,000			.7999

are based on the formula for density given in I. C. T.:

$$\text{Density} = 0.82390 - 0.699 \times 10^{-3}t - 0.32 \times 10^{-6}t^2.$$

Normal-hexyl Alcohol. This was obtained from Kahlbaum; it was evidently not entirely pure, because it was of a slight yellow color. On the first set-up, runs were attempted at 0° and 50°. On the first run at 0° freezing was encountered, but the amount was so slight that I hoped the sylphon had not been damaged. The results with decreasing pressure at 50°, however, strongly suggested a leak, and on taking the apparatus apart a crease was found in one of the folds of the sylphon which was doubtless the result of the freezing at 0°. A second set-up was therefore made with a new sylphon, and three successful runs at 0°, 50°, and 95°, and the return check readings were obtained without incident. The average departure from smooth curves of a single one of the 39 readings was 0.50% of the

maximum effect, considerably larger than usual, but in large part accounted for by the smaller range.

The relative volumes are given in Table XVIII. In making the

TABLE XVIII.

RELATIVE VOLUMES OF N-HEXYL ALCOHOL

Pressure	Temperature		
kg./cm.²	0°	50°	95°
0	1.0000		
500	.9719	1.0078	
1,000	.9488	.9791	1.0052
1,500	.9316	.9583	.9813
2,000	.9183	.9420	.9619
2,500	.9075	.9278	.9467
3,000		.9159	.9337
4,000		.8960	.9118
5,000		.8787	.8931
6,000			.8773
7,000			.8637

calculations the density at atmospheric pressure at 0° was assumed to be 0.8204, this being the figure given in Landolt and Börnstein. The thermal expansion has apparently not been recorded in the literature, and no attempt is made to give values for it in the table.

In addition to these results on new liquids, certain measurements were made on other liquids during the preliminary testing of the apparatus which are worth recording.

Ether. This material was from Mallinckrodt, reagent quality, but it had been standing in a cork stoppered bottle for some time and may have absorbed moisture. The runs with this material were the first successful ones in which the sylphon was carried through a complete cycle without leak. Ether was chosen as the liquid because previous experience had shown that among easily obtainable liquids this, or CS_2, most readily disclosed a leak. In order to check further the reliability of the method, the compressibility of ether was determined numerically, and compared with the results of the previous method. The temperatures for this comparison were chosen as 30° and 75°, which are within the range of the previous work, whereas 0° and 95° both lie outside the previous range. Since the purpose was only comparative, pressure at 75° was not lowered below 2400 kg, the manipulations in this way being somewhat easier. In this preliminary

exploration special attention was also given to the method proposed for getting the thermal expansion, the temperature being changed back and forth several times between 30° and 75°. The check here was perfect; it was possible to return exactly to the same isotherm after leaving it at any pressure in the range. The average departure from smooth curves of a single one of the 32 readings was 0.08% of the maximum effect.

In calculating the results the formula given in I. C. T. for the density was used:

$$\text{Density} = 0.73629 - 1.1138 \times 10^{-3}t - 1.237 \times 10^{-6}t^2.$$

The relative volumes are given in Table XIX, and in parallel columns

TABLE XIX.

RELATIVE VOLUMES OF ETHER.

Pressure	Temperature			
	30°		75°	
kg./cm.²	new	previous	new	previous
0	1.0495	*1.0492*		
500	.9761	*.9790*		
1,000	.9364	*.9445*		
1,500	.9085	*.9153*		
2,000	.8858	*.8980*		
2,500	.8671	*.8734*	.8909	*.8970*
3,000	.8511	*.8576*	.8726	*.8788*
4,000	.8255	*.8318*	.8446	*.8496*
5,000	.8055	*.8111*	.8225	*.8268*
6,000	.7888	*.7954*	.8038	*.8098*
7,000	.7742	*.7806*	.7884	*.7940*
8,000	.7616	*.7675*	.7747	*.7800*
9,000	.7504	*.7554*	.7629	*.7672*
10,000	.7399	*.7444*	.7519	*.7560*
11,000	.7305	*.7335*	.7418	*.7457*
12,000	.7225	*.7237*	.7329	*.7353*

in italics the values previously found. The agreement is not by any means as good as could be desired; the maximum discrepancy in the volume is about 0.006 in the neighborhood of 3000 kg. At the maximum pressure the difference becomes much less. It is important to notice that the thermal expansions of the two series differ from the mean by only a few per cent, so that the fundamental question

about the functioning of the new apparatus was thereby answered satisfactorily.

These preliminary measurements could be regarded as satisfactory in establishing most of the questionable points with regard to the new method, but in view of the uncertainty introduced by the unknown purity of the ether, did not answer the question as to the consistency of the absolute values obtained by the two methods. Subsequently another attempt was made to check the absolute values by using a liquid easily obtained in sufficient purity. For this purpose water was chosen. From one point of view the test with water was particularly severe, because it is one of the least compressible of liquids.

Water. This was distilled water of ordinary laboratory purity; it would have been useless to have started with conductivity water in view of the fact that it was to be placed in contact immediately with a metal. The three regular runs at 0° 50°, and 95° and the return check readings were made without incident. Except for one discarded point, which was so far from the curve that a blunder in reading is indicated, the average departure from smooth curves of a single one of the remaining 44 points was 0.15%.

The relative volumes are given in Table XX, with the previous values at 0° and 50° for comparison in italics; the previous range

TABLE XX.

RELATIVE VOLUMES OF WATER.

Pressure	Temperature				
	0°		50°		95°
kg./cm.²	new	previous	new	previous	new
0	1.0000				
500	.9771				
1,000	.9567	*.9578*	.9741	*.9743*	.9984
1,500	.9396	*.9424*	.9582	*.9586*	.9812
2,000	.9248	*.9260*	.9439	*.9445*	.9661
3,000	.8996	*.9015*	.9201	*.9205*	.9409
4,000	.8795	*.8807*	.8997	*.8996*	.9194
5,000	.8626	*.8632*	.8824	*.8818*	.9009
6,000			.8668	*.8662*	.8849
7,000			.8530	*.8524*	.8705
8,000			.8407	*.8399*	.8577
9,000			.8296	*.8288*	.8461
10,000			.8192	*.8188*	.8352
11,000					.8256

extended only to 80° so that comparison at 95° is not possible. Because of danger of freezing, no measurements were made at atmospheric pressure at 0°, and in making the calculations the fiducial volume was chosen as that at 500 kg and 0°, using the value 0.9771 obtained in the previous measurements. The agreement is seen to be much closer than for ether, and in particular the agreement at 50° is as good as could be desired. In view of the fact that the new data cover a wider range than the old I think that perhaps the new values should be given the preference, although this is a difficult question.

Finally, during the preliminary examination of the method, an attempt was made to find whether consistent results for compressibility could be obtained irrespective of the amount of liquid in the sylphon. If the cross section is truly independent of the extension of the sylphon, then the compressibility obtained with it should be independent of the amount of liquid in the sylphon, that is, independent of the initial extension of the sylphon. In order to make this test it is obviously necessary to choose a relatively incompressible liquid, because the compression of the more compressible liquids is so great as to use all available stroke of the sylphon. An incompressible liquid has the disadvantage of giving relatively small effects, and so enhancing the error from slight irregularities; there seemed, however, no way of avoiding this source of error.

Glycerine and water. The liquid chosen for this test was a mixture of equal parts by volume of water and glycerine, the glycerine being Kahlbaum's purest. Pure glycerine is much less compressible than water, but its viscosity increases so much under pressure that fear was felt for the safety of the sylphon had it been used pure. The comparison with two fillings of the sylphon was made only at 30°. The compressibilities and dimensions of the apparatus were such that a difference in the two initial amounts of about 25% was possible. Two runs were made with the larger filling, the initial points of the first being irregular, perhaps because the changes of pressure were made too rapidly for this rather viscous liquid. The decreasing points of this run and the second run gave regular points. A single run with the second filling was sufficient, the points lying smoothly. The average departure from a smooth curve of a single one of the 22 readings with the larger filling was 0.44%, and of the 11 readings with the smaller filling 0.25%.

The ratio of the changes of volume obtained with the two fillings

should be a constant, independent of pressure. The following values were found for the ratio at successive intervals of 1000 kg, from 1000 to 11000 kg respectively: 1.236, 1.223, 1.230, 1.238, 1.250, 1.259, 1.265, 1.265, 1.265, 1.268, 1.268, 1.266. The ratio is therefore effectively constant beyond 6000 kg. Below 6000, greater deviation would be expected because the effects are absolutely smaller and the chance for relative error greater. In fact, on making a detailed examination of the experimental points, it will be seen that the deviation at the lower pressures is not more than can be accounted for by the irregularity of the experimental points, so that these measurements may be considered to give satisfactory proof of the fact that even under pressure the effective cross section of the sylphon is independent of its extension.

The actual values of the compressibility of the glycerine-water mixture are of some interest, and are given in Table XXI. The

TABLE XXI.

COMPRESSION OF 50 PER CENT GLYCERINE-WATER MIXTURE AT 30° C.

Pressure kg./cm.^{2}	Loss of volume in cm.^{3} per gm.
1,000	.0291
2,000	.0521
3,000	.0715
4,000	.0886
5,000	.1033
6,000	.1159
7,000	.1279
8,000	.1385
9,000	.1479
10,000	.1569
11,000	.1651

density of the mixture was not specially measured, so that the results are best given as loss of volume in cm.^{3} per gm. of mixture. The average of the two fillings is given.

DISCUSSION.

This discussion will touch only some of the main qualitative features of the situation; no attempt will be made to extend the elaborate discussion of the former paper on twelve liquids to these new liquids. All the information to be obtained from these new

measurements is implicitly contained in the tables of volumes, from which any one may extricate for himself any information important for his particular purposes.

The new data of this paper allow a very considerable extension in one respect of the information of the previous paper, that is, with regard to the behavior of isomers at high pressures. In the previous list of 12 liquids there were only two isomeric compounds, that is, compounds with the same chemical formula, namely ether and butyl alcohol ($C_4H_{10}O$). These are, however, so different in structure that the chemist is not usually inclined to think of them as isomers. The fact previously found was that the volume of ether and butyl alcohol tends to become more nearly the same at high pressures, the ratio of the volumes of the same number of grams, that is, of the same number of molecules, being 1.106 at 500 kg and 1.038 at 12000 kg at 50. This seems the natural behavior, and it was my expectation that the new data would act in the same way. The number of isomers between which comparison may be made is now considerably increased, there being normal- and iso- propyl alcohols, normal- and iso- butyl alcohols, normal- and iso- pentane, and the 5 isomeric hexanes. These substances are more nearly what the chemist usually thinks of as isomers, the structural differences not being so great as between ether and butyl alcohol.

It turns out that the rule found for ether and butyl alcohol is not followed by these new isomers, but the volume differences between equal weights of the various pairs or sequences of isomers follows no rule. The relations are brought out in the following tables, in which the volumes of equal weights of different isomers are compared at a temperature of 50°. In Table XXII the relative volumes of the

TABLE XXII.

VOLUMES OF EQUAL WEIGHTS OF ISOMERIC ALCOHOLS AT 50° C.

Pressure	Propyl Alcohols			Butyl Alcohols		
	Volume of .8179 gm.			Volume of .8239 gm.		
kg./cm.²	normal-	iso-	Ratio	normal	iso-	Ratio
0	1.0493	1.0756	1.0250	1.0455	1.0508	1.0051
2,000	.9293	.9487	1.0209	.9372	.9336	.9962
4,000	.8813	.8945	1.0149	.8867	.8791	.9914
6,000	.8494	.8588	1.0111	.8530	.8445	.9900
8,000	.8250	.8327	1.0093	.8269	.8197	.9913
10,000	.8060	.8114	1.0067	.8076	.7996	.9901
12,000	.7905	.7944	1.0049		.7821	

propyl and butyl alcohols are shown. The ratio of the volumes of the two forms of propyl alcohol approaches more closely to unity at high pressure than at atmospheric pressure, according to expectation, but the reverse is true for the butyl alcohols. The iso- form of propyl alcohol has a larger volume than the normal form over the entire pressure range, whereas the iso- form of butyl alcohol has a larger volume than the normal form at atmospheric pressure, but at high pressures has the smaller volume. The normal form of both alcohols is seen to have a smaller compressibility than the iso- form. In Table XXIII the volumes of equal weights of normal and iso- pentane

TABLE XXIII.

VOLUMES OF EQUAL WEIGHTS OF PENTANES AT 50°

Pressure	Volume of .6454 gm.		
kg./cm.²	normal-	iso-	Ratio
0	1.0837	1.0924	1.0080
2,000	.8820	.8911	1.0103
4,000	.8193	.8283	1.0110
6,000	.7807	.7909	1.0131
8,000	.7520	.7649	1.0172
9,000	.7409	.7530	1.0163

are compared. Iso-pentane has throughout the greater volume, and the difference becomes greater at high pressures than at atmospheric pressure. This means that the normal form of pentane has greater average compressibility than the iso-form, unlike the alcohols. In Table XXIV the volumes of 1 gm. of the isomeric hexanes are given,

TABLE XXIV.

VOLUMES OF 1 GM. OF ISOMERIC HEXANES AT 50°.

Pressure	Volumes					Ratio to n-hexane			
kg/ cm.²	Normal hexane	2-methyl pentane	3-methyl pentane	2.2-dimethyl butane	2.3-dimethyl butane	2-methyl pentane	3-methyl pentane	2.2-dimethyl butane	2.3-dimethyl butane
0	1.5827	1.5973	1.5697		1.5750	1.0092	.9918		.9951
2,000	1.3363	1.3357	1.3125	1.3470	1.3160	.9996	.9897	1.0080	.9851
4,000	1.2517	1.2470	1.2260	1.2647	1.2313	.9962	.9794	1.0104	.9837
6,000	1.1953	1.1940	1.1743	1.2113	1.1793	.9989	.9824	1.0134	.9866
8,000	1.1550	1.1537	1.1357		1.1380	.9989	.9833		.9853
10,000	1.1250	1.1217	1.1037		1.1030	.9971	.9810		.9804
12,000	1.1008*		1.0790				.9802		

* Extrapolated.

and the ratios to the volume of n-hexane. With the exception of 2-methyl pentane, the volumes of these isomers are more different from the normal form at high pressures than at atmospheric pressure, again contrary to expectation. In general, the compressibility of those compounds is greatest in which the CH_2 radical occupies a 3-position.

In contrast to the previous example of ether and butyl alcohol, the phenomena shown by these isomers are on a much smaller scale, and the volumes are always much more nearly equal. In view of this, I do not believe that the fact that the volumes of these new isomers do not in general tend toward greater equality at high pressures need alter the conclusion previously drawn, namely that because of the compressibility of the molecules there is a tendency to equality of volumes at high pressures. It is obvious however that the comparatively small structural differences of these new isomers persist, and may even become more prominent up to pressures of 12000 kg. Other lines of evidence have already suggested that there are conditions under which liquids may approach a greater semblance of order at high pressures, a fact which is not inconsistent with the discovery by X rays of structure in liquids under ordinary conditions.

Another instructive comparison is afforded by the volumes of the series of normal hydro-carbons, comparing the volumes per gm. molecule. In Table XXV are shown the volumes at 50° of 1 gm.

TABLE XXV.

VOLUME OF 1 GM. MOLECULE OF NORMAL HYDRO-CARBONS AT 50°.

Pressure kg./cm.²	Pentane		Hexane		Heptane		Octane		Decane
0	121.03	*15.24*	136.27	*15.63*	151.90	*16.37*	168.27	*32.40*	200.67
2,000	98.51	*16.54*	115.05	*14.72*	129.77	*16.33*	146.10	*30.50*	176.60
4,000	91.52	*16.25*	107.77	*13.80*	121.57	*15.63*	137.20	*28.93*	166.13
6,000	87.20	*15.73*	102.93	*13.44*	116.37	*14.70*	131.07		
8,000	83.99	*15.46*	99.45	*13.08*	112.53				
10,000	81.72	*15.15*	96.87	*12.58*	109.45				

molecule of the normal hydro-carbons as a function of pressure, together with the successive differences, in italics, on passing from one member of the series to another. In the first place, there are very distinct differences between the odd and even members of the series, the increase of volume when a CH_2 group is added on passing from an odd to an even member being greater than the increase on passing from an even to an odd member. The only exception to this is at atmospheric pressure between pentane and hexane; here there is a

special effect. 50° is above the boiling point of pentane, and the volume listed was obtained by extrapolation of the volumes at considerably lower temperatures; the volume so obtained accentuates too much the larger volume of the approaching vapor phase in comparison with the other hydro-carbons, so that the difference between pentane and hexane is too small. The difference between odd and even steps in the series becomes less in going to higher members of the series, but becomes greater on going to higher pressures. This again is not what might at first be expected, and reminds one of the behavior of the isomers. It means that the first effect of high pressure is to accentuate the effect of structural differences in the molecules, in virtue of which they are perhaps squeezed into some semblance to an orderly arrangement. It is already known from X-ray investigations that there are differences between the volumes occupied in the solid crystal form by the odd and even members of the series, and Müller (7) has been able to give a detailed account of this in terms of the shapes of the molecules.

Pass now from a consideration of the volume to the compressibility. The most striking fact found for the previous twelve liquids was the very great decrease of compressibility with increasing pressure, the compressibility at 12000 kg being on the average about 1/15th of the compressibility at atmospheric pressure. This continues to be the fact for these new liquids, and what is more, the details of behavior are the same, in that the compressibility has dropped to about half its initial value in the first thousand kilograms, the rate of decrease becoming slower, until at 6000 pressure must be raised another 6000, that is, from 6000 to 12000, to reduce the compressibility again by a factor of 2.

The compressibilities do not vary through a very wide range, as may be seen by plotting the relative volumes of the various liquids in a single diagram. Of the new liquids, n-pentane is the most compressible. The compressibility in general decreases in a series of compounds on passing in the direction of increasing molecular weight. Thus in the series of normal hydro-carbons, the compressibility of decane is of the order of two-thirds that of pentane; in the series C_6H_6, C_6H_5Cl, C_6H_5Br, the compressibility decreases in the order given. Of the organic liquids previously examined, glycerine stood in a class by itself, with the smallest compressibility. Then came water, also in a class by itself, with a compressibility of the order of twice that of glycerine, and then the twelve liquids, with a compressi-

bility on the average perhaps 50% greater than that of water, although the initial compressibilities were much more than 50% greater. Most of the new liquids fall in the same group as the preceding twelve, but there are two, C_6H_5Cl and C_6H_5Br, which fall in the same class as water; in fact the curves of relative volume of these three liquids very nearly coincide. The compressibility of C_6H_6, on the other hand, is about 60% greater than that of its two substitution products. This very large difference seems surprising. The difference is without doubt due in part to the effect so often discussed by Professor T. W. Richards:[8] the cohesive forces in C_6H_5Cl and C_6H_5Br must be fairly high, as shown by a consideration of the molecular volumes, for the increase of volume on passing from C_6H_6 to C_6H_5Cl and C_6H_5Br is of the order of half the molecular volume of free (solid) Cl or Br, and this means a high internal pressure and small compressibility. But the matter is not as simple as this, because the compressibilities of C_6H_5Cl and C_6H_5Br are very nearly the same, whereas the atomic compression on passing from C_6H_6 to C_6H_5Cl is materially less than on passing to C_6H_5Br.

It is evident that there is an interesting field for future investigation in seeking out organic compounds with abnormally small compressibility; the unique position of glycerine has as yet received no explanation.

The thermal expansion next concerns us. In the previous work on twelve liquids two important facts stood out with regard to thermal expansion; the thermal expansion at 12000 kg is almost always 4 or 5 times smaller than at atmospheric pressure, and at a pressure of a few thousand kilograms there is a reversal of sign of $\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$, that is, at low pressures the thermal expansion increases with increasing temperature, but at high pressures it decreases with increasing temperature. The new data of this paper are not sufficient to give as much detail about thermal expansion as the preceding data because of the smaller number of temperature intervals, but they are adequate on these two important points. The decrease of thermal expansion with increasing pressure is larger on the average in the series of hydrocarbons than for the preceding twelve liquids; thus for pentane the decrease is by a factor of 7, and for n-hexane by 8. Many of the new data do not extend over as wide a pressure range as the preceding because of freezing, so that a complete comparison cannot be made; the two new isomeric alcohols fall in line with the previous results. The ratio for C_6H_5Cl and C_6H_5Br is smaller than the previous average.

The second important previous feature, the reversal of sign of $\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$, is also shown by all of these new liquids in which the pressure range attainable at 0° was extensive enough to provide the requisite data. The pressure at which the reversal takes place is also roughly the same as before, that is, in the neighborhood of 2000 or 3000 kg. In the series of hydro-carbons the pressure of reversal tends to become less as the molecular weight increases. Among the isomers of hexane there are some striking examples of strong reversal. 3-methyl pentane is perhaps the most striking: at atmospheric pressure the mean expansion 50°–100° (obtained by increasing the tabulated difference 50°–95° by 11%) is 22.7% greater than the mean expansion between 0° and 50°, whereas at 11000 kg it is 40.7% less. The fact that this reversal of sign is now found again with this fundamentally different apparatus affords welcome presumptive evidence of the essential correctness of the results obtained by both methods.

The suggestion has been made in a previous publication[9] that the probable reason for this reversal is that at high pressures and low temperatures the molecules are crowded so close together that the departures from linearity of the forces between molecules must be greater than at higher temperatures at the same pressure (that is, at larger volumes), since it is known that a large thermal expansion goes with a large departure from linearity, the thermal expansion of a substance with a linear law of force being zero.

Considerable importance attaches to the "pressure coefficient" $\left(\frac{\partial p}{\partial \tau}\right)_v$; the suggestion has been made a number of times that this should be a function of volume only, or an equivalent statement is that at constant volume, pressure is a linear function of temperature. In the previous paper on 12 liquids I showed that this does not agree with the experimental facts, and detailed calculations were presented for CS_2 from which it appeared that $\left(\frac{\partial p}{\partial \tau}\right)_v$ was a complicated function of temperature at constant volume. The theoretical reasons for thinking $\left(\frac{\partial p}{\partial \tau}\right)_v$ to be a volume function only have, however, appealed to some writers as strong enough to justify them in ascribing the complicated variations there found to experimental irregularities, and in continuing to assume that the theoretical relation is correct.

The new data of this paper allow a more decisive inquiry as to the validity of this relation, because the temperature intervals are fewer and wider, thus smoothing out small scale irregularities. The question may at once be answered from the graphs showing volume as

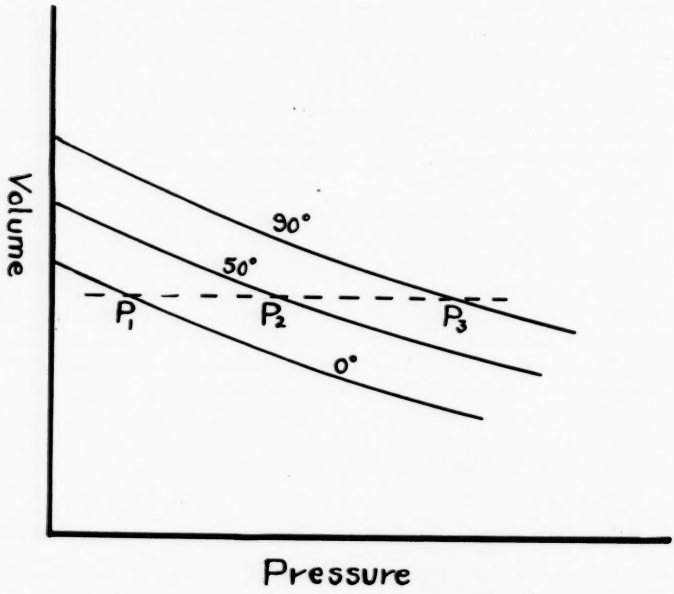

FIGURE 4. Graphical construction for finding whether $\left(\frac{\partial p}{\partial \tau}\right)_v$ is a function of volume only.

a function of pressure at 0°, 50°, and 95°. If $\left(\frac{\partial p}{\partial \tau}\right)_v$ is constant on a line of constant volume then $p_3 - p_2$ should be to $p_2 - p_1$ as 45 to 50, that is $\frac{p_3 - p_2}{p_2 - p_1}$ should equal 0.90 (Fig. 4). This ratio has been calculated at a number of points for many of the liquids of this paper, and the results are shown in Table XXVI. In making the calcula-

TABLE XXVI.

TEST OF THE INDEPENDENCE OF $\left(\frac{\partial p}{\partial \tau}\right)_v$ OF TEMPERATURE AT CONSTANT VOLUME.

Substance	Value of ratio $\left(\frac{p_3 - p_2}{p_2 - p_1}\right)_v$					
	Rel. vol.	ratio	Rel. vol.	ratio	Rel. vol.	ratio
n-pentane	.92	.84 ±	.75	.98		
i-pentane	.94	.905	.80	.972		
n-hexane	.92	.95 ±	.79	.774		
2-methyl pentane	.94	.897	.80	.910		
3-methyl pentane	.94	.865	.80	.817	.75	.597
2–2-dimethyl butane	.92	.743	.82	.68		
2–3-dimethyl butane	.95	.895	.80	.747		
n-heptane	.99	.914	.82	.832		
n-octane	.99	.806	.87	.767		
n-decane	.94	.837				
C_6H_5Cl	.95	.893				
C_6H_5Br	.95	.870				
i-propyl alcohol	.96	.947	.86	.925	.79	.900
n-butyl alcohol	.96	.837	.86	.850		
n-hexyl alcohol			.80	.845		

tions, the figures given in the tables of relative volume were used by linear interpolation; this accounts for the irregular volumes used, which were so chosen as to be as near as possible to the integral pressures of the tables, thus minimizing the small errors from linear interpolation. Table XXVI shows many deviations of the ratio from 0.90 which are far beyond any experimental error. The ratio usually starts with a value fairly near 0.90 at volumes near 1, that is, at low pressures, but as volume decreases, the ratio nearly always decreases, which means that at high pressures $\left(\frac{\partial p}{\partial \tau}\right)_v$ decreases with increasing temperature at constant volume. This was also the general nature of the results previously found for CS_2. There are, however, a few exceptions to this rule, n- and i- pentane being especially conspicuous for the large increase of the ratio on passing from larger to smaller volumes.

It is worth while to examine a little further the implications in assuming $\left(\frac{\partial p}{\partial \tau}\right)_v$ is a volume function only. If this is the case, integration gives at once

$$p = \tau f(v) + \varphi(v),$$

where f and φ are two arbitrary volume functions. The physical meaning of this equation is easy to see; it states that the pressure exerted by a fluid can be regarded as arising from two mechanisms acting independently of each other. One part, $\varphi(v)$, is a pure volume effect, in virtue of which a fluid exerts as much pressure at any temperature as it would at 0° Abs. at the same volume. This part of the pressure may be thought of as arising from the attractive or repulsive forces between the molecules. The second part is a kinetic part, proportional to absolute temperature, and arising from the change of momentum in unit time of the molecules as they collide with the walls. In a perfect gas, elementary considerations show that the momentum change in unit time is proportional to the kinetic energy, that is, to the temperature, and the volume function, f, becomes very simple. If the molecules have a finite size, f becomes more complicated. The nature of the two terms is clearly shown in van der Waals' equation, which satisfies the demand that $\left(\frac{\partial p}{\partial \tau}\right)_v$ be a function of volume only, and which may be written in the form $p = \tau \frac{R}{v-b} - \frac{a}{v^2}$, where the volume function $\frac{R}{v-b}$ arises from the finite size of the molecules, and $\frac{a}{v^2}$ arises from the mutual attractions.

But van der Waals' equation certainly is not correct at high pressures, in that it omits, among other things, the very important factor of the compressibility of the molecules. In fact, one can expect in general that the hypothesis that there are two mechanisms, each acting independently of the other with no interaction effects, can be valid only over a narrow range in which the forces are approximately linear in the changes of volume, and in particular cannot be expected to hold at high pressures where there are certainly departures from linearity. That such is the case may be shown in detail in one very simple case. In the preceding paper on 12 liquids is worked out in detail the characteristic equation of the simplest conceivable substance, consisting of a single molecule. This molecule was, however, deformable, so that during collision with the walls it exerts pressure through an elastic mechanism which could be completely specified. Any ordinary liquid must have features in its mechanism closely corresponding to this. Within a certain range, which alone need concern us here, the characteristic equation of this substance consisting of a single molecule had the form

$$p\{v - b + a\tau^{1/2}\} = 2\tau,$$

where b gives the undeformed size of the molecule, and a depends on its elasticity. This equation is not of the general form given above, and gives at once:

$$\left(\frac{\partial p}{\partial \tau}\right)_v = \frac{2(v-b) + a\tau^{1/2}}{[(v-b) + a\tau^{1/2}]^2}.$$

This is evidently not a function of volume only, and in fact becomes smaller at higher temperature at constant volume. This corresponds to the fact brought out in Table XXVI that in general the ratio $\frac{p_3 - p_2}{p_2 - p_1}$ is less than 0.9. I believe that this feature of the mechanism must be present to a greater or less extent in any actual liquid, and that we are not to expect $\left(\frac{\partial p}{\partial \tau}\right)_v$ to be a volume function only, particularly at high pressures.

Another closely connected topic discussed in the former paper was concerned with the connection between internal energy and volume. Normally, as volume decreases with increasing pressure at constant temperature the internal energy decreases, but eventually passes through a minimum at a pressure equal to $\tau\left(\frac{\partial p}{\partial \tau}\right)_v$, and at higher pressures increases. The interpretation is that at ordinary volumes and temperatures the intermolecular forces are on the average attractive, and at small volumes (high pressures) repulsive; the volume at which $\left(\frac{\partial E}{\partial p}\right)_\tau = 0$ is the volume at which the attractive and the repulsive forces balance. Now at 0° Abs at atmospheric pressure the two sets of forces are in equilibrium, so that if the parts played by the various mechanisms are additive, the volume at which $\left(\frac{\partial E}{\partial p}\right)_\tau$ becomes 0 at room temperature would be expected to be equal to the volume at 0° Abs at atmospheric pressure. I have already examined this question for the solid metals[10] and found, as might be expected, that the critical volume at room temperature is not equal to that at 0° Abs at atmospheric pressure, but in general is less, so that the mechanisms cannot be additive. Recently Hildebrand[11] has applied the same idea to liquids, using in his discussion the data which I had obtained for ether. Most of the others of the twelve liquids were highly polar, and might, therefore, be expected to have complications.

Hildebrand found that the volume at which $\left(\frac{\partial E}{\partial p}\right)_\tau$ becomes 0 for ether at room temperature is very nearly, as well as can be judged from other data, its volume at 0° Abs at atmospheric pressure. Hildebrand also found the same state of affairs approximately for mercury. The liquids of this paper are normal enough to justify an examination of this point for them. In the case of n-pentane, $\left(\frac{\partial E}{\partial p}\right)_\tau = 0$ when relative volume is equal 0.77. The volume at 0° Abs at atmospheric pressure, calculated from the density of the solid[12] by the same argument that Hildebrand used for ether, is 0.80.

It should be noted that these considerations can be good only to the extent that $\left(\frac{\partial p}{\partial \tau}\right)_v$ is a pure volume function, and that therefore they cannot be expected to apply exactly to the liquids of this paper.

Summary.

A new method of measuring compressibility and thermal expansions of liquids has been developed, in which the liquid is enclosed in a sylphon, which is then exposed to external hydrostatic pressure, and the volume change determined from the change of length of the sylphon. This method has been applied to 18 liquids at 0°, 50°, and 95° up to a pressure of 12000 kg, or to the freezing pressure, and the results are collected into extensive tables giving the volume as a function of pressure aand temperature over this range. In the discussion it is shown that small scale differences in the volumes of various isomers persist to high pressures, and there is no simple connection between the relative densities at atmospheric pressure and at high pressure. The compressibility falls off rapidly with rising pressure, as was found in a preceding investigation. Two liquids are found to have the abnormally low compressibility of water. Thermal expansion also drops off by a large factor with increasing pressure, but not as much as the compressibility, as was also found before. The "pressure coefficient" $\left(\frac{\partial p}{\partial \tau}\right)_v$, is not a function of volume only, as has often been supposed, and suggestions are made as to the theoretical significance of this.

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REFERENCES 1.

[1] P. W. Bridgman, Proc. Amer. Acad. 44, 1, 1915.
[2] P. W. Bridgman, ZS. f. Krist. 67, 363, 1928.
[3] P. W. Bridgman, Proc. Amer. Acad. 56, 63, 1921.
[4] P. W. Bridgman, Proc. Amer. Acad. 58, 191, 1923.
[5] Harry Essex, Dissertation, Göttingen, 1914.
[6] A. and J. Shuman, Jour. Amer. Chem. Soc. 50, 1118, 1928.
[7] A. Müller, Proc. Roy. Soc. 120, 437, 1928; 124, 317, 1929.
[8] T. W. Richards, Jour. Chim. Phys. 25, 83, 1928.
[9] P. W. Bridgman, Handbuch der Exp. Phys. vol. 8, part II, p. 308.
[10] Reference 9, page 284.
[11] Joel H. Hildebrand, Phys. Rev. 34, 984, 1929.
[12] J. C. McLennan and W. G. Plummer, Trans. Roy. Soc. Can. 21, 99, 1927.